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(54) **Unleaded gasoline for direct injection gasoline engine**

(57) An unleaded gasoline for a direct injection gasoline engine contains an oxygen-containing compound having 2-15 carbon atoms in an amount in terms of oxygen atom of 0.1-15 mass % based on the total

gasoline. The inventive unleaded gasoline exhibits enhanced durability of an engine due to the capability of reducing the amount of exhaust smoke and suppressing smoldering of a spark plug as well as the formation of deposit in a combustion chamber.

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Description

[0001] This invention relates to unleaded gasolines for use in direct injection gasoline engines and more particularly to such a gasoline which is capable of reducing the amount of environmental pollutants emission and further excellent in durability of the engine in which the gasoline is employed.

[0002] From the viewpoint of resource-savings and suppression of global warming, it has been a world-wide demand that the usage of fossil fuel should be decreased and in connection with this an improvement in fuel consumption becomes the most important issue for gasoline-engine automobiles. On the other hand, there are some urban areas which fail to achieve the environmental standards in terms of the amount of pollutants such as NO_x (nitrogen oxide), and gasoline-engine automobiles are thus required to be less in the amount of such pollutants emission. A direct injection gasoline engine is considered to be the most effective means for meeting or satisfying such a demand or standard.

[0003] A conventional engine forms a homogeneous pre-mixture of gasoline and air by injecting gasoline into the intake port, while a direct injection gasoline engine injects gasoline directly into the combustion chamber like a diesel engine so that it becomes possible to form a stratified fuel mixture which is rich in the neighborhood of the spark plug but ultra highly lean in the entire combustion chamber. Due to the formation of such a stratified fuel mixture, combustion with the highly lean mixture can be achieved, leading to an improvement in fuel consumption equivalent to that of a diesel engine. Moreover, the direct injection of gasoline into the combustion chamber is contributive to the freedom of delay in gasoline vaporization as seen in the conventional engine and enables further enhanced accuracy in control of fuel injection rate.

[0004] However, the direct injection gasoline engine would be encountered with some unexpected problems which are different from those of the conventional engines due to the direct injection of gasoline into the combustion chamber. One of such problems is related to the smoke exhausted mainly from the part of the mixture in which the gasoline is excessively rich, upon the stratified combustion. This smoke contained in exhaust gases not only adversely affects the environment but also causes smoldering of the spark plug, leading to deterioration of durability of the engine.

[0005] In view of the foregoing problems, the present invention is intended to provide an unleaded gasoline suitable for a direct injection gasoline engine which gasoline is capable of reducing the amount of environmental pollutants emission and further improving durability of the engine.

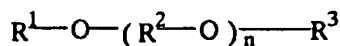
[0006] It has now been found after extensive research that the amount of exhaust smoke can be reduced by use of an unleaded gasoline containing an oxygen-containing compound in a predetermined amount for a direct injection gasoline engine, resulting in suppression of smoldering of the spark plug and the formation of deposits in the combustion chamber thereby improving durability of the engine.

[0007] According to the present invention, there is provided an unleaded gasoline for a direct injection gasoline engine which contains an oxygen-containing compound having 2-15 carbon atoms in an amount in terms of oxygen atom of 0.1-15 mass % based on the total gasoline.

[0008] The unleaded gasoline for a direct injection gasoline engine according to the invention contains an oxygen-containing compound having 2-15, preferably 2-12, more preferably 2-10 carbon atoms.

[0009] There is no particular limitation imposed on the structure of the oxygen-containing compound as long as it has 2-15 carbon atoms in the molecule. Generally, such an oxygen-containing compound has in its molecule at least one oxygen-containing group selected from the group consisting of a hydroxyl group, an ether bond and a carbonyl group.

[0010] An oxygen-containing compound eligible for the present invention is represented by the formula



(I)

wherein R¹ and R³ each are hydrogen or a C₁ - C₁₅ hydrocarbon group, R² is a C₂ - C₄ alkylene group and n is an integer of 0 - 7, provided that the total carbon number in the molecule is from 2 to 15 and if n is 0, it is excluded that both R¹ and R³ are hydrogen at the same time.

[0011] Each of R¹ and R³, independently the other, is hydrogen or a C₁ - C₁₅ hydrocarbon but is preferably hydrogen or a C₁ - C₁₃ straight or branched alkyl group, a C₂ - C₁₃ straight or branched alkenyl group, a C₅ - C₁₃ cycloalkyl or alkylcycloalkyl group, a C₆ - C₁₃ aryl or alkylaryl group or a C₇ - C₁₃ arylalkyl group. Preferred alkyl groups for R¹ and R³ include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, straight or branched pentyl, straight or branched hexyl, straight or branched heptyl, straight or branched octyl, straight or branched nonyl, straight or branched decyl, straight or branched undecyl, straight or branched dodecyl and straight or branched tridecyl.

[0012] Preferred examples of an alkenyl group for R^1 and R^3 include vinyl, propenyl, isopropenyl, straight or branched butenyl, butadienyl, straight or branched pentenyl, straight or branched hexenyl, straight or branched heptenyl, straight or branched octenyl, straight or branched nonenyl, straight or branched decenyl, straight or branched undecenyl, straight or branched dodecenyl and straight or branched tridecenyl groups.

[0013] Preferred examples of a cycloalkyl group for R^1 and R^3 include cyclopentyl, cyclohexyl and cycloheptyl groups while preferred examples of an alkylcycloalkyl groups include methylcyclopentyl, dimethylcyclopentyl (inclusive of all positional isomers), ethylcyclopentyl (inclusive of all positional isomers), straight or branched propylcyclopentyl (inclusive of all positional isomers), ethylmethylcyclopentyl (inclusive of all positional isomers), trimethylcyclopentyl (inclusive of all positional isomers), diethylcyclopentyl (inclusive of all positional isomers), ethyldimethylcyclopentyl (inclusive of all positional isomers), straight or branched propylmethylcyclopentyl (inclusive of all positional isomers), straight or branched propylethylcyclopentyl (inclusive of all positional isomers), di(straight or branched) propylcyclopentyl (inclusive of all positional isomers), straight or branched propylethylmethylcyclopentyl (inclusive of all positional isomers), methylcyclohexyl (inclusive of all positional isomers), dimethylcyclohexyl (inclusive of all positional isomers), ethylcyclohexyl (inclusive of all positional isomers), straight or branched propylcyclohexyl (inclusive of all positional isomers), ethylmethylcyclohexyl (inclusive of all positional isomers), trimethylcyclohexyl (inclusive of all positional isomers), diethylcyclohexyl (inclusive of all positional isomers), ethyldimethylcyclohexyl (inclusive of all positional isomers), straight or branched propylmethylcyclohexyl (inclusive of all positional isomers), straight or branched propyl ethyl cyclohexyl (inclusive of all positional isomers), di-straight or branched propylcyclohexyl (inclusive of all positional isomers), straight or branched propylethylmethylcyclohexyl (inclusive of all positional isomers), methylcycloheptyl (inclusive of all positional isomers), dimethylcycloheptyl (inclusive of all positional isomers), ethylcycloheptyl (inclusive of all positional isomers), straight or branched propylcycloheptyl (inclusive of all positional isomers), ethylmethylcycloheptyl (inclusive of all positional isomers), trimethylcycloheptyl (inclusive of all positional isomers), diethylcycloheptyl (inclusive of all positional isomers), ethyldimethylcycloheptyl (inclusive of all positional isomers), straight or branched propylmethylcycloheptyl (inclusive of all positional isomers), straight or branched propylethylcycloheptyl (inclusive of all positional isomers), di-straight or branched propylcycloheptyl (inclusive of all positional isomers) and straight or branched propylethylmethylcycloheptyl groups (inclusive of all positional isomers).

[0014] Preferred examples of an aryl group for R^1 and R^3 include phenyl and naphthyl groups, while preferred examples of an alkylaryl group include tolyl (inclusive of all positional isomers), xylyl (inclusive of all positional isomers), ethylphenyl (inclusive of all positional isomers), straight or branched propylphenyl (inclusive of all positional isomers), ethyl methyl phenyl (inclusive of all positional isomers), trimethylphenyl (inclusive of all positional isomers), straight or branched butylphenyl (inclusive of all positional isomers), straight or branched propyl methyl phenyl (inclusive of all positional isomers), diethylphenyl (inclusive of all positional isomers), ethyldimethylphenyl (inclusive of all positional isomers), tetramethylphenyl (inclusive of all positional isomers), straight or branched pentylphenyl (inclusive of all positional isomers), straight or branched hexylphenyl (inclusive of all positional isomers) and straight or branched heptylphenyl (inclusive of all positional isomers).

[0015] Among of these, R^1 and R^3 each independently are preferably hydrogen or a $C_1 - C_{12}$ straight or branched alkyl group, more preferably hydrogen or a $C_1 - C_6$ straight or branched alkyl group and most preferably hydrogen or $C_1 - C_4$ straight or branched alkyl group.

[0016] R^2 in formula (I) is a $C_2 - C_4$ alkylen group such as ethylene, propylene (1-methylethylene, 2-methylethylene), trimethylene, butylene (1-ethylethylene, 2-ethylethylene), 1,2-dimethylethylene, 2,2-dimethylethylene, 1-methyltrimethylene, 2-methyltrimethylene, 3-methyltrimethylene and tetramethylene among which ethylene, propylene and butylene are preferred.

Formula (I) wherein either R^1 or R^2 is hydrogen, the other is a hydrocarbon and n is 0 represents a monohydric alcohol. Such an alcohol is exemplified by a monohydric aliphatic alcohol which may be straight or branched. Specific examples of the monohydric aliphatic alcohol include ethanol, straight or branched propanol, straight or branched butanol, straight or branched pentanol, straight or branched hexanol, straight or branched heptanol, straight or branched octanol, straight or branched nonanol, straight or branched decanol, straight or branched undecanol, straight or branched dodecanol, straight or branched tridecanol, straight or branched tetradecanol, straight or branched pentadecanol and mixtures thereof. Preferred among the above monohydric aliphatic alcohol are those having 2 - 12 carbon atoms, more preferred are those having 2 - 10 carbon atoms and most preferred are those having 2 - 6 carbon atoms because they are particularly excellent in an reduction in exhausted smoke. Methanol is not preferred because it would increase aldehyde concentration in the exhaust gas and is corrosive.

Formula (I) wherein R^1 and R^2 each are a hydrocarbon group and n is 0 represents an ether. Such an ether compound exemplarily includes dimethylether, methyl ethyl ether, diethylether, methyl propylether (inclusive of all isomers of propyl group), ethyl n -propylether (inclusive of all isomers of propyl group), dipropylether, methylbutylether (inclusive of all isomers of butyl group), ethylbutylether (inclusive of all isomers of propyl group), propylbutylether (inclusive of all isomers of propyl group and butyl group), dibutylether (inclusive of all isomers of butyl group), methylpentylether (inclusive of all isomers of pentyl group), ethylpentylether (inclusive of all isomers of pentyl group), pro-

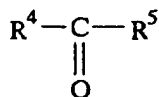
pylpentylether (inclusive of all isomers of propyl group and pentyl group), butylpentylether (inclusive of all isomers butyl group and pentyl group) and dipentylether (inclusive of all isomers of pentyl group). Preferred among the above ethereal compounds are those having 2 - 12 carbon atoms, more preferred are those having 3 - 10 carbon atoms and most preferred are those having 4 - 8 carbon atoms because of an excellent effect in a reduction of exhaust smoke.

[0017] Represented by formula (I) wherein R^1 and R^3 each are hydrogen and n is an integer of more than 1 is a dihydric alcohol. Specific examples of such a dihydric alcohol include ethylene glycol, propylene glycol, 1,3-propane diol, 1,2-butane diol (butylene glycol), 1,3-butane diol, 1,4-butane diol, 2-methyl-1,2-propane diol, 2-methyl-1,3-propane diol, 1,2-pentane diol, 1,3-pentane diol, 1,4-pentane diol, 1,5-pentane diol, neopentyl glycol and polymers thereof.

[0018] Represented by formula (I) wherein at least one of R^1 and R^3 is a hydrocarbon group and n is an integer of more than 1 is a compound obtained by etherifying at least one of the two terminal hydroxyl groups of the above-mentioned dihydric alcohol. Such a terminal-etherified compound exemplarily include ethylene glycol monoalkylether, ethylene glycol dialkylether, propylene glycol monoalkylether, propylene glycol dialkylether, butylene glycol monoalkylether, butylene glycol dialkylether, diethylene glycol monoalkylether, diethylene glycol dialkylether, dipropylene glycol monoalkylether, dipropylene glycol dialkylether, dibutylene glycol monoalkylether and dibutylene glycol dialkylether.

[0019] Although not encompassed by compounds represented by formula (I), polyhydric alcohols having three or more hydroxyl groups can be used as the oxygen-containing compound defined by the present invention. Such alcohols are those having 3 - 10, preferably 3 - 6 hydroxyl groups. Specific examples of the alcohol having 3 - 10 hydroxyl groups are polyhydric alcohols such as glycerol, polyglycerol (dimers through pentamers of glycerol such as diglycerol, triglycerol and tetraglycerol), trimethylolalkane (trimethylolethane, trimethylolpropane and trimethylolbutane) and the dimers and trimers thereof, pentaerythritol and the dimers and trimers thereof, 1,2,4-butanetriol, 1,3,5-pentanetriol, 1,2,6-hexanetriol, 1,2,3,4-butanetetrol, sorbitol, sorbitan, sorbitol glycerin condensation products, adonitol, arabitol, xylitol and mannitol; and saccharides such as xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose and sucrose; and mixtures thereof.

[0020] The oxygen-containing compound having in its molecule a carbonyl group may be exemplified by ketones and esters. Such ketones can be represented by the formula



(II)

wherein R^4 and R^5 are each independently a $C_1 - C_{13}$ hydrocarbon group, provided that the total carbon number of R^4 and R^5 is from 2 to 14.

[0021] Preferred hydrocarbon groups for each R^4 and R^5 are a $C_1 - C_{13}$ straight or branched alkyl group, a $C_2 - C_{13}$ straight or branched alkenyl group, a $C_5 - C_{13}$ cycloalkyl or alkylcycloalkyl group, a $C_6 - C_{13}$ aryl or alkylaryl group or a $C_7 - C_{13}$ arylalkyl group all of which have been exemplified with respect to R^1 and R^3 . R^4 and R^5 each are more preferably a $C_1 - C_{12}$ straight or branched alkyl group. Further more preferably, R^4 and R^5 each are a $C_1 - C_6$ straight or branched alkyl group and most preferably are a $C_1 - C_4$ alkyl group.

[0022] Specific examples of the ketones represented by formula (II) include dimethylketone (acetone), methyl ethylketone, diethyl ketone, methyl propyl ketone (inclusive of all isomers of propyl group), ethylpropylketone (inclusive of all isomers of propyl group), dipropyl ketone (inclusive of all isomers of propyl group), methylbutylketone (inclusive of all isomers of butyl group), ethylbutylketone (inclusive of all isomers of butyl group), propylbutylketone (inclusive of all isomers of propyl and butyl groups), dibutylketone (inclusive of all isomers of butyl group), methylpentylketone (inclusive of all isomers of pentyl group), ethylpentylketone (inclusive of all isomers of pentyl group), propylpentylketone (inclusive of all isomers of propyl and pentyl groups), butylpentylketone (inclusive of all isomers of butyl and pentyl groups) and dipentylketone (inclusive of all isomers of pentyl group).

[0023] Although not encompassed by formula (II), a cyclic ketone such as cyclohexane and the like is also eligible for the inventive oxygen-containing compound.

[0024] There may be used an alcohol which may be monohydric or polyhydric and an acid which may be monobasic or polybasic for the ester used as the oxygen-containing compound.

[0025] Preferred monohydric alcohols may be those having 1 - 10 carbon atoms, more preferred are those having 1 - 6 carbon atoms and most preferred are those having 1 - 4 carbon atoms. Specific examples of the monohydric alcohol having 1 - 10 carbon atoms are methanol, ethanol, straight or branched propanol, straight or branched butanol, straight or branched pentanol, straight or branched hexanol, straight or branched heptanol, straight or branched octanol, straight or branched nonanol, straight or branched decanol, straight or branched undecanol, straight or branched undecanol,

straight or branched dodecanol, straight or branched tridecanol, straight or branched tetradecanol, straight or branched pentadecanol and mixtures thereof.

[0026] Alternatively, an alkoxyalcohol having 2 - 14, preferably 2 - 10, more preferably 2 - 6 carbon atoms is also eligible. Specific examples of such an alkoxy alcohol are methoxymethyl alcohol, methoxyethyl alcohol, ethoxyethyl alcohol, methoxypropyl alcohol (inclusive of all isomers of propyl group), ethoxypropyl alcohol (inclusive of all isomers of propyl group), propoxypropyl alcohol (inclusive of all isomers of propyl group), methoxybutyl alcohol (inclusive of all isomers of butyl group), ethoxybutyl alcohol (inclusive of all isomers of butyl group) and methoxypentyl alcohol (inclusive of all isomers of pentyl group).

[0027] Eligible polyhydric alcohols are the dihydric alcohols and polyhydric alcohols having 3 or more hydroxyl groups which are exemplified as being preferred for the compound represented by formula (I).

[0028] Eligible monobasic acids are fatty acids having 2 -14 carbon atoms. Such fatty acids may be straight or branched and saturated or unsaturated. Specific examples of the fatty acids are saturated fatty acids such as ethanoic acid (acetic acid), straight or branched propanoic acid, straight or branched butanoic acid, straight or branched heptanoic acid, straight or branched hexanoic acid, straight or branched heptanoic acid, straight or branched octanoic acid, straight or branched nonanoic acid, straight or branched decanoic acid, straight or branched undecanoic acid, straight or branched dodecanoic acid, straight or branched tridecanoic acid, straight or branched tetradecanoic acid; and unsaturated aliphatic acids such as straight or branched propenoic acid (acrylic acid), straight or branched butenoic acid (inclusive of methacrylic acid), straight or branched heptenoic acid, straight or branched hexenoic acid, straight or branched heptenoic acid, straight or branched octenoic acid, straight or branched nonenoic acid, straight or branched decenoic acid, straight or branched undecenoic acid, straight or branched dodecenoic acid, straight or branched tridecenoic acid and straight or branched tetradecenoic acid; and mixtures thereof. Among these fatty acids, preferred are saturated fatty acids having 2 - 10 carbon atoms, more preferred are saturated fatty acids having 2 - 6 carbon atoms and most preferred are saturated aliphatic acids having 2 - 4 carbon atoms.

[0029] Eligible polybasic acids are dibasic acids having 2 -13 carbon atoms and trimellitic acid. These dibasic acids having 2 -13 carbon atoms may be straight or branched and saturated or unsaturated. Specific examples of such dibasic acids are saturated dibasic acids such as ethanedioic acid (oxalic acid), propanedioic acid (oxalic acid), straight or branched butanedioic acid (inclusive of succinic acid), straight or branched pentanedioic acid, straight or branched hexanedioic acid, straight or branched heptanedioic acid, straight or branched octanedioic acid, straight or branched nonanedioic acid, straight or branched decanedioic acid, straight or branched undecanedioic acid, straight or branched dodecanedioic acid and straight or branched tridecanedioic acid; and unsaturated dibasic acid such as straight or branched butenedioic acid (inclusive of maleic acid and fumaric acid), straight or branched pentenedioic acid, straight or branched hexenedioic acid, straight or branched heptenedioic acid, straight or branched octenedioic acid, straight or branched nonenedioic acid, straight or branched decenedioic acid, straight or branched undecenedioic acid, straight or branched dodecenedioic acid and straight or branched tridecenedioic acid; and mixtures thereof. Preferred among these polybasic acids are dibasic acids having 2 - 10 carbon atoms. More preferred are dibasic acids having 2 - 6 carbon atoms and most preferred are dibasic acids having 2 - 4 carbon atoms.

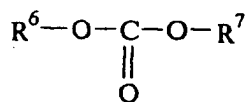
[0030] The esters used as the inventive oxygen-containing compound may constituted by any combinations of an alcohol and an acid. Such combinations are exemplified as follows:

- (1) an ester of a monohydric alcohol and a monobasic acid,
- (2) an ester of a polyhydric alcohol and a monobasic acid,
- (3) an ester of a monohydric alcohol and a polybasic acid,
- (4) an ester of a polyhydric alcohol and a polybasic acid,
- (5) a mixed ester of a mixture of a monohydric alcohol and a polyhydric alcohol and a polybasic acid,
- (6) a mixed ester of a polyhydric alcohol and a mixture of a monobasic acid and a polybasic acid, and
- (7) a mixed ester of a mixture of a monohydric alcohol and a polyhydric alcohol and a mixture of a monobasic acid and polybasic acid.

[0031] If a polyhydric alcohol is used as an alcohol component, the ester obtained may be a full ester derived from the complete esterification of all of the hydroxyl groups contained in the polyhydric alcohol or a partial ester having one or more of hydroxyl groups remaining unesterified. If a polybasic acid is used as an acid component, the ester may be a full ester derived from the complete esterification of all of the carboxyl groups in the polybasic acid or a partial ester having one or more of carboxyl groups remaining unesterified.

[0032] An alcohol and an acid forming the ester used as the inventive oxygen-containing compound has individually been described. Preferred esters are methyl acetate, ethyl acetate, propyl acetate (inclusive of all isomers of propyl group), butyl acetate (inclusive of all isomers of butyl group), methoxypropyl acetate (inclusive of all isomers of propyl group), dimethyl succinate, diethyl succinate, dimethyl maleate and diethyl maleate.

[0033] Besides the above-described ester, there may be used a carbonic ester represented by the formula



(III)

wherein R⁶ and R⁷ are each independently a C₁ - C₁₃ hydrocarbon group provided that the total carbon number of R⁶ and R⁷ is from 2 to 14.

[0034] Preferred hydrocarbon groups for each R⁶ and R⁷ are a C₁ - C₁₃ straight or branched alkyl group, a C₂ - C₁₃ straight or branched alkenyl group, a C₅ - C₁₃ cycloalkyl or alkylcycloalkyl group, a C₆ - C₁₃ aryl or alkylaryl group or a C₇ - C₁₃ arylalkyl group all of which has been exemplified with respect to R¹ and R³, R⁶ and R⁷ each are preferably a straight or branched C₁ - C₁₂ alkyl group, more preferably a straight or branched C₁ - C₆ alkyl group and most preferably a straight or branched C₁ - C₄ alkyl group.

[0035] Specific examples of the carbonic ester represented by formula (III) are dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate (inclusive of all isomers of propyl group), ethylpropyl carbonate (inclusive of all isomers of propyl group), dipropyl carbonate (inclusive of all isomers of propyl group), methylbutyl carbonate (inclusive of all isomers of butyl group), ethylbutyl carbonate (inclusive of all isomers of butyl group), propylbutyl carbonate (inclusive of all isomers of propyl and butyl groups), dibutyl carbonate (inclusive of all isomers of butyl group), methylpentyl carbonate (inclusive of all isomers of pentyl group), ethylpentyl carbonate (inclusive of all isomers of pentyl group), propylpentyl carbonate (inclusive of all isomers of propyl and pentyl groups), butylpentyl carbonate (inclusive of all isomers of butyl and pentyl groups) and dipentyl carbonate (inclusive of all isomers of pentyl group).

[0036] Furthermore, besides the above-exemplified esters, a cyclic ester such as γ -butyrolactone is also eligible for the oxygen-containing compound according to the invention.

[0037] In the present invention, the oxygen-containing compound may be used singular or in combination.

[0038] The unleaded gasoline according to the invention contains, based on the total weight thereof, the above-described oxygen-containing compound in an amount in terms of oxygen atom of more than 0.1 mass %, preferably more than 0.7 mass %, more preferably more than 1.5 mass % and most preferably more than 2 mass % and less than 15 mass %, preferably less than 10 mass %, more preferably less than 8 mass %. The content of the oxygen-containing compound if less than the lower limit of 0.1 mass % would not be sufficient in a reduction of the amount of the exhaust smoke, while the content in excess of the upper limit of 15 mass % would not be expected in further enhancement and would lead to the possibility of an increase in fuel consumption and an increase in NO_x emission.

[0039] The content of the oxygen-containing compound itself is not particularly restricted as long as the content thereof by oxygen atomic conversion falls within the range of 0.1 - 15 mass %. However, the oxygen-containing compound content should be greater than 0.3 mass %, preferably greater than 1 mass %, based on the total mass of the gasoline because a further reduction in the amount of the exhaust smoke can be expected.

[0040] The inventive gasoline is substantially free of alkyl lead compounds such as tetraethyl lead, but should such compounds be present, the amount thereof should be held below the lower threshold specified by JIS K2255 related to the test method for lead in gasolines.

[0041] Although the inventive gasoline is not restricted to octane number, it should have an octane number of greater than 89, preferably greater than 90, more preferably greater than 90.5 and most preferably greater than 91 by the research octane number (RON), and an octane number of greater than 80, preferably greater than 80.5 and most preferably greater than 81 by the motor octane number (MON) so as to maintain good anti-knock performance.

[0042] Both RON and MON octane numbers are values measured by the test procedure of JIS K 2280 "Testing Method for Octane Number and Cetane Number".

[0043] The distillation properties of the inventive gasoline pursuant to the test method of JIS K 2254 "Testing Method for Distillation of Petroleum Products" should be as follows:

Running point at 10 vol. % (T₁₀)... 35 - 55°C
 Running point at 30 vol. % (T₃₀) ... 55 - 75°C
 Running point at 50 vol. % (T₅₀) ... 75 - 100°C
 Running point at 70 vol. % (T₇₀) ... 100 - 130°C
 Running point at 90 vol. % (T₉₀) ... 120 - 160°C
 End point ... 130 - 210°C

[0044] Lower limit temperature (T₁₀) is 35°C, preferably 40°C. Below 35°C would cause gasoline coking in an injector. Upper limit temperature (T₁₀) is 55°C, preferably 50°C, more preferably 48°C. Above 55°C would lead to aggravated low temperature engine startability.

[0045] Lower limit temperature (T_{30}) is 55°C, preferably 60°C. Below 55°C would invite objectionable high temperature engine performance and cause gasoline coking in an injector. Upper limit temperature (T_{30}) is 75°C, preferably 70°C, more preferably 68°C. Above 75°C would lead to aggravated low temperature engine performance.

[0046] Lower limit temperature (T_{50}) is 75°C, preferably 80°C. Below 75°C would adversely affect engine performance at low and normal temperatures. Upper limit temperature (T_{50}) is 100°C, preferably 95°C, more preferably 93°C. Above 100°C would lead to aggravated high temperature engine performance.

[0047] Lower limit temperature (T_{70}) is preferably 100°C. Upper limit temperature (T_{70}) is 130°C, preferably 125°C, more preferably 123°C, most preferably 120°C. Above 130°C would lead to aggravated normal temperature engine performance.

[0048] Upper limit temperature (T_{90}) is 160°C, preferably 150°C, more preferably 140°C. The upper limit of less than 160°C leads to a reduction in engine oil dilution and prevents an increase in exhaust smoke, deterioration in the engine oil and the formation of sludges. Lower limit temperature (T_{90}) is preferably greater than 120°C.

[0049] Lower limit end point is preferably 130°C, while upper limit is 210°C, preferably 200°C, more preferably 195°C and most preferably 190°C. End point in excess of 210°C would lead to aggravated normal temperature engine performance.

[0050] Though not restricted, the Reid vapor pressure (RVP) of the inventive gasoline as defined by JIS K 2258 "Testing Method for Vapor Pressure of Petroleum Products (Reid Method)" should be less than 70 kPa, preferably less than 65 kPa, more preferably less than 60 kPa and most preferably less than 55 kPa to preclude the possibility of gasoline coking in the injector and suppress the amount of evaporative emission.

[0051] Though not restricted, the density at 15°C of the inventive gasoline should preferably be in the range of 0.73 to 0.77 g/cm³. The lower limit of densities is 0.73 g/cm³, preferably 0.735 g/cm³. Densities below 0.73 g/cm³ would result in increased fuel consumption. The upper limit of density is 0.77 g/cm³, preferably 0.76 g/cm³. Densities above 0.77 g/cm³ would lead to the possibility of insufficient acceleration and spark plug smoldering.

[0052] The term "density" used herein designate a density determined by JIS K 2541 resting Method for Densities of Crude Oil and Petroleum Products and Density-Mass-Volume Conversion Table".

[0053] Although the inventive gasoline is not restricted in terms of the contents of paraffins, olefins and aromatics, such contents should preferably be in the following range:

| | |
|-------------------|----------------------|
| Paraffins (V(P)) | 50 - 100 % by volume |
| Olefins (V(O)) | 0 - 15 % by volume |
| Aromatics (V(Ar)) | 0 - 35 % by volume |

[0054] The content of V(P) in the inventive gasoline should be in the range of 50 - 100 % by volume, preferably 60 - 100 % by volume, more preferably 70 - 100 % by volume with a view to precluding gasoline coking in the injector, reducing spark plug smoldering and ozone-formability of the exhaust gas as well as the benzene concentration thereof, with a freedom from soot.

[0055] The content of V(O) in the inventive gasoline should be in the range of 0 - 15 % by volume, preferably 0 - 10 % by volume, more preferably 0 - 7 % by volume, most preferably 0 - 5 % by volume with a view to preventing gasoline coking in the injector.

[0056] The content of V(Ar) in the inventive gasoline should be in the range of 0 - 35 % by volume, preferably 0 - 30 % by volume, more preferably 0 - 100 % by volume, most preferably 0 - 20 % by volume with a view to precluding gasoline coking in the injector, reducing spark plug smoldering and ozone-formability of the exhaust gas as well as the concentrates of benzene thereof, with a freedom from soot.

[0057] The contents of the above paraffins, olefins and aromatics are measured by the procedure of JIS K 2536 resting Method for Hydrocarbon Types in Petroleum Products by Fluorescent Indicator Adsorption".

[0058] The inventive gasoline is not restricted in terms of the content of each component other than the oxygen-containing compound which however should be in the following range.

(1) V(Bz) : 0 - 1 % by volume

(2) V(Tol) : 0 - 30 % by volume

(3) V(C₈A) : 0 - 20 % by volume

(4) V(C₉A) : 0 - 5 % by volume

(5) V(C₁₀+A) : 0 - 3 % by volume

(6) V(PA) = 0 or

when V(PA) ≠ 0, V(MA)/V(PA) : more than 1

(7) V(C₄) : 0 - 10 % by volume

(8) V(C₅) : 10 - 35 % by volume

- (9) V(C₆) : 10 - 30 % by volume
 (10) V(C₇⁺p) : 10 - 50 % by volume
 (11) V(C₇⁺) : 10 - 50 % by volume

5 [0059] V(Bz) is the amount of benzene, based on the total gasoline. The amount of the benzene should be in the range of 0 - 1 % by volume, preferably 0 - 0.5 % by volume. The benzene in an amount of 0 - 1 % by volume results in the reduced concentrate of benzene in the exhaust gas.

[0060] V(Tol) and V(G₈A) are the amount of toluene and the amount of a C₈ aromatic hydrocarbon, based on the total gasoline, respectively. V(Tol) should be in the range of 0 - 30 % by volume, preferably 0 - 20 % by volume, while
 10 V(C₈A) should be in the range of 0 - 20 % by volume, preferably 0 - 15 % by volume. The C₈ aromatic hydrocarbon includes ethylbenzene and xylene (inclusive of all positional isomers).

[0061] V(C₉A) is the amount of a C₉ aromatic hydrocarbon, based on the total gasoline. V(C₉A) should be in the range of 0 - 5 % by volume, preferably 0 - 3 % by volume with a view to reducing the formability of ozone in the exhaust gas. The C₉ aromatic hydrocarbon exemplarily include n-propylbenzene, isopropylbenzene (cumene), ethylmethylbenzene (inclusive of all positional isomers) and trimethylbenzene (inclusive of all positional isomers).

15 [0062] V(C₁₀⁺A) is the amount of the aromatic hydrocarbon having more than 10 carbon atoms, based on the total gasoline. V(C₁₀⁺A) should be in the range of 0 - 3 % by volume, preferably 0 - 1 % by volume but more preferably be held to 0 % by volume. The aromatic hydrocarbon having more than 10 carbon atoms exemplarily includes diethylbenzene (inclusive of all positional isomers), dimethylethylbenzene (inclusive of all positional isomers), tetramethylbenzene (inclusive of all positional isomers) and n-butylmethylbenzene (inclusive of all positional isomers).

20 [0063] V(MA) and V(PA) are the amount of the aromatic hydrocarbon having one alkyl substituent (% by volume) and the amount of the aromatic hydrocarbon having more than 2 alkyl substituents (% by volume), based on the total gasoline. In the present invention, if V(PA) is 0 or V(MA) is not 0, the ratio of V(PA) to V(MA) should be held more than 1, preferably 1.5, more preferably more than 2.

25 [0064] The above V(Bz), V(Tol), V(C₈A), V(C₉A), V(C₁₀⁺A), V(C₉⁺), V(MA) and V(PA) are determined by the procedure of JIS K 2536 "Testing Method for Hydrocarbon Types in Petroleum Products by Gas Chromatography".

[0065] V(C₄) is the amount of a C₄ hydrocarbon, based on the total gasoline. V(C₄) should be in the range of 0 - 10 % by volume, preferably 0 - 5 % by volume, more preferably 0 - 3 % by volume with a view to further reducing the amount of evaporative emission. The C₄ hydrocarbon exemplarily includes n-butane, 2-methylbutane (isobutane),
 30 1-butene, 2-butene and 2-methylpropene.

[0066] V(C₅) is the amount of a C₅ aliphatic hydrocarbon, based on the total gasoline. The lower limit of V(C₅) should be 10 % by volume, preferably 15 % by volume, while the upper limit should be 35 % by volume, preferably 30 % by volume. The C₅ aliphatic hydrocarbon content more than 10 % by volume is contributive to the production of an unleaded gasoline excelled in engine performance at normal temperatures. The C₅ aliphatic hydrocarbon content less than 35 % by volume leads to an unleaded gasoline improved in high temperature engine performance. When a consideration given to the preclusion of gasoline coking in the injector, it is desired that the unsaturated hydrocarbon content (V(C₅o)) (volume %) in the C₅ aliphatic hydrocarbon is 0, or the ratio of the saturated hydrocarbon content (V(C₅p)) (volume %) in the C₅ aliphatic hydrocarbon to V(C₅o), that is, (V(C₅p))/(V(C₅o)), is more than 1, preferably more than 1.5, more preferably more than 2, most preferably 3. The C₅ unsaturated aliphatic hydrocarbon exemplarily includes n-pentane, 2-methylbutane (isopentane), and 2,2-dimethylpropane (neopentane), while the C₅ saturated aliphatic hydrocarbon exemplarily includes 1-pentene, 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene and 3-methyl-1-butene.

[0067] V(C₆) is the amount of a C₆ aliphatic hydrocarbon, based on the total gasoline. The lower limit of the C₆ aliphatic hydrocarbon content is 10 % by volume, preferably 15 % by volume, while the upper limit is 30 % by volume, preferably 25 % by volume. The C₆ aliphatic hydrocarbon content greater than 10 % by volume results in the production of an unleaded gasoline excelled in normal temperature engine performance, while the same less than 30 % by volume leads to the production of an unleaded gasoline further improved in high temperature engine performance. In view of prevention in gasoline coking in the injector, it is desired that the unsaturated hydrocarbon content (V(C₆o)) (volume %) in the C₆ aliphatic hydrocarbon is 0, or the ratio of the saturated hydrocarbon content (V(C₆p)) (volume %) in the C₆ aliphatic hydrocarbon to V(C₆o), that is, (V(C₆p))/(V(C₆o)), is more than 2, preferably more than 3, more preferably more than 5, most preferably 10. The C₆ saturated aliphatic hydrocarbon exemplarily includes n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane, while the C₆ unsaturated aliphatic hydrocarbon exemplarily includes 1-hexene, 2-hexene, 3-hexene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl-2-pentene, 3-methyl-2-pentene, 4-methyl-2-pentene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene and 2,3-dimethyl-2-butene.

55 [0068] V(C₇⁺p) is the amount of a saturated aliphatic hydrocarbon having more than 7 carbon atoms, based on the total gasoline. The lower limit of V(C₇⁺p) is 10 % by volume, preferably 20 % by volume, while the upper limit of the same is 50 % by volume, preferably 45 % by volume. V(C₇⁺p) greater than 10 % by volume leads to an unleaded gasoline excelled in normal temperature engine performance, while V(C₇⁺p) less than 50 % by volume leads to an

unleaded gasoline excelled in high temperature engine performance. The saturated aliphatic hydrocarbon of more than 7 carbon atoms exemplarily includes n-heptane, 2-methylhexane, 3-methylhexane, 2,2-dimethyl pentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 3-ethylpentane and 2,2,3-trimethylbutane.

[0069] (C_9^+) is the amount of a hydrocarbon having more than 9 carbon atoms, based on the total gasoline. (C_9^+) is in the range of 0 - 10 % by volume, preferably 0 - 5 % by volume. By reducing the amount of the aliphatic compound having more than 9 carbon atoms, it makes it possible to reduce the amount of gasoline which dilutes the engine oil thereby reducing the amount of the exhaust hydrocarbon, preventing the engine oil from deterioration and precluding sludge formation.

[0070] The above $V(C_4)$, $V(C_5)$, $V(C_5p)$, $V(C_5o)$, $V(C_6)$, $V(C_6p)$, $V(C_6o)$, $V(C_7^+p)$ and $V(C_9^+)$ are as determined by gas chromatography. Analysis is made with the use of a methyl silicone-made capillary column, a helium or nitrogen carrier gas and an FID detector under a set of condition of 25 to 50 mm in length, 0.5 to 1.5 ml/min in gas flow rate, 1: 50 to 1:250 in partition ratio, 150 to 250°C in inlet temperature, -10 to 10°C in initial column temperature, 200 to 250°C in end column temperature and 150 to 250°C in detector temperature.

[0071] No particular limitation is imposed upon the sulfur content of the inventive gasoline, which however is less than 50 ppm, preferably less than 30 ppm, more preferably 20 ppm, most preferably less than 10 ppm, based on the total gasoline. This content if larger than 50 ppm would be responsible for poisoning an after treatment catalyst, increases of the concentrations of NOx, Co and Hc and a sharp rise in benzene emission.

[0072] The term "sulfur content" used herein refers to a sulfur content measured by the method of JIS K 2541 "Testing Method for Sulfur in Crude Oil and Petroleum Products".

[0073] The unwashed existing gum and washed gum of the inventive gasoline should be in an amount of less than 20 mg/100 ml and an amount of less than 3 mg/100 ml, preferably less than 1 mg/100 ml, respectively as measured by the method of JIS K.2261 "Testing Method for Existing Gum of Petroleum Products, Motor Gasolines and Aviation Fuels by Spray Evaporation". Deviations from these amounts would lead to the formation of deposits in the fuel-induction system and the occurrence of agglutination in the intake valve.

[0074] The gross calorific value of the inventive gasoline should be more than 35,000 J/g, preferably 40,000 J/g, more preferably 45,000 J/g as measure by JIS K 2279 "Testing and Calculation Methods for Gross Calorific Value of Crude Oil and Petroleum Products".

[0075] The oxidation stability of the inventive gasoline should be over 480 minutes, preferably over 1,440 minutes as measured by the method of JIS K 2287 "Testing Method for Gasoline Oxidation Stability (Induction Period Method)". Oxidation stability less than 480 minutes would lead to the formation of gum during storage.

[0076] The inventive gasoline should exhibit 1 or less the value of the copper corrosion test conducted in accordance with the procedure of JIS K 2513 "Copper Corrosion Test of Petroleum Products (at a temperature of 50°C for 3 hours)". Copper corrosion exceeding 1 would cause corrosion of the pipe of the fuel system.

[0077] The kerosene content of the inventive gasoline should be in the range of 0 - 4 % by volume, based on the total gasoline. The kerosene content referred herein means the content of a C_{13} - C_{14} hydrocarbon (% by volume) as quantitatively determined by the gas chromatographic process in which a methyl-silicone caterpillar column having a column length of 25 - 50 m is fed with a helium or nitrogen gas at a flow rate of 0.5 - 1.5 ml/min and a divisional ratio of 1:50 - 1:250 and operated at an inlet temperature of 150 - 250°C and at initial column temperature of -10 - 10°C and final column temperature of 150 - 250°C, and a hydrogen ion detector is operated at 150 - 250°C.

[0078] No particular restriction is imposed upon the production method for the unleaded gasoline of the invention. There may be used any suitable known base gasolines such as light naphtha derivable by atmospheric distillation of crude oil, cracked gasoline derivable by catalytic cracking or hydrocracking, reformed gasoline obtainable by catalytic reforming, polymerized gasoline available by olefin polymerization, alkylates derivable addition reaction or alkylation of a hydrocarbon such as isobutane with a lower olefin, isomerized gasoline derivable by converting light naphtha into isoparaffin using an isomerization device, de-n-paraffinized oil, butane, aromatic hydrocarbons and paraffinic fractions derivable by hydrocracking dimerized propylene.

[0079] A typical blend formulation of the inventive unleaded gasoline is shown below.

- (1) reformed gasoline : 0 - 70 vol. %
- (2) light fractions of reformed gasoline
(boiling at 25 - 120°C) : 0 - 35 vol. %
- (3) heavy fractions of reformed gasoline
(boiling at 110 - 200°C) : 0 - 45 vol. %
- (4) cracked gasoline : 0 - 50 vol. %
- (5) light fractions of cracked gasoline
(boiling at 25 - 90°C) : 0 - 45 vol. %
- (6) alkylate : 0 - 40 vol. %
- (7) paraffin fraction derived from dimerizing and subsequently hydrogenating propylene : 0 - 30 vol. %

- (8) isomerized gasoline : 0 - 30 vol. %
- (9) light naphtha : 0 - 10 vol. %
- (10) butane : 0 - 10 vol. %
- (11) oxygen-containing compound : 0.3 - 30 vol. %

[0080] Upon production of the inventive unleaded gasoline, any suitable methods can be employed to reduce the benzene content in the inventive gasoline, one example of such methods being to add smaller amount of reformed gasoline containing a large amount of benzene. Alternatively, the benzene-content reduction can be achieved by using reformed gasoline having been subjected to treatments for reducing the benzene content. Such treatments are as follows :

- (1) removing benzene fraction by distilling reformed gasoline,
- (2) extracting benzene from reformed gasoline with sulfur or like solvents,
- (3) converting benzene into other compounds by a method such as

- (A) conversion into cyclohexane, methylcyclopentane and the like via hydrogenation of benzene,
- (B) conversion into toluene, xylene, ethylbenzene and the like via reaction of benzene with C₉ or greater aromatic hydrocarbon, or
- (C) alkylation of benzene with lower olefins such as ethylene and propylene or with lower alcohols such as methanol and ethanol

- (4) using as a reformer feed of desulfurized heavy naphtha derived by removing C₆ hydrocarbons by distillation, and
- (5) controlling the operation conditions of a catalytic reforming apparatus.

[0081] In a direct injection gasoline engines, there is a risk that due to the injector being subjected to increased temperatures, the gasoline therein is coked by its denaturation, leading to an increase in combustion chamber deposition (CCD). Therefore, the inventive unleaded gasoline should be added with detergent additives such as succinic acid imide, polyalkyl amine and polyetheramine so as to prevent injector coking and reduce CCD. Preferred for such detergent additives are those which are free of residues after being subject to thermal decomposition at 300°C in the air. The amount of the above additives is less than 1 % by volume, preferably less 0.1 % by volume, based on the total gasoline.

[0082] There may be used some conventional fuel additives exemplarily including antioxidants such as phenol- or amine- ones, metallic inactivating agents such as Schiff-type compounds or thioamide-type compounds, surface ignition preventers such as organophosphorus-derived compounds, combustion adjuvants such as alkali metal or alkaline earth metal salts of organic acids and sulfuric esters of higher alcohols, antistatic agents such as anionic surfactants, cationic surfactants and amphoteric surfactants, colorants such as azo dyes, rust preventives such as alkenyl succinate, identify agents such as quinizarin and coumarin and malodorants such as natural essential-based aromatics. These may be used in combination but preferably in an amount of less than 0.1 % by mass, based on the total gasoline.

[0083] The invention will be further described by way of the following examples which however should not be construed in a limiting sense.

[0084] There was prepared a variety of base gasolines each having the composition and properties as indicated in Table 1.

Inventive Examples 1 - 6 and Comparative Examples 1 and 2

[0085] Sample gasolines for Inventive and Comparative Examples were prepared by blending the base gasolines in accordance with the blending ratio indicated in Table 2. The composition and properties of each sample gasoline are shown in Table 2.

[0086] Each of the sample gasolines thus obtained was evaluated in performance by the following automotive tests.

Automotive Test 1

[0087] Using a diesel smoke meter, smoke exhaustion was measured on an automobile installed with a 1.8-liter displacement, direct injection gasoline engines. During the test, the automobile was kept to run at a constant speed of 40 km/h.

Automotive Test 2

[0088] A 2.0-liter displacement, direct injection gasoline engine was operated at a oil-water temperature of 60 °C under the condition equivalent to the constant running at a speed of 40 km/h for 150 hours and thereafter the dilution of the engine oil by the gasoline was measured.

[0089] As described above, the inventive unleaded gasoline contains a specified oxygen-containing compound in a definite amount thereby reducing the amount of exhaust smoke and suppressing smoldering of the spark plug and the formation of deposit in the combustion chamber, leading to improved engine durability.

Table 1

| | | (A) base gasoline | (B) base gasoline | (C) MTBE | (D) TAE | (E) MPA |
|---|-----------------------|-------------------|-------------------|----------|---------|---------|
| RON | | 100.2 | 102.9 | 118 | 111 | 53 |
| MON | | 88.7 | 89.9 | 101 | 95 | 40 |
| Distillation properties (°C) | Initial Boiling Point | 30.0 | 30.5 | | | |
| | T10 | 48.5 | 51.5 | | | |
| | T30 | 69.5 | 78.5 | | | |
| | T50 | 98.0 | 111.5 | | | |
| | T70 | 118.0 | 134.0 | | | |
| | T90 | 140.0 | 162.5 | | | |
| | End Point | 174.5 | 176.0 | | | |
| RVP (kPa) | | 75.0 | 70.0 | 53.3 | 12.5 | 2.0 |
| density (g/cm ³) | | 0.757 | 0.775 | 0.747 | 0.770 | 0.970 |
| Composition (vol. %) | aromatics | 33 | 43 | 0 | 0 | 0 |
| | olefins | 9 | 9 | 0 | 0 | 0 |
| | paraffins | 58 | 49 | 0 | 0 | 0 |
| | Bz | 0.7 | 0.5 | 0 | 0 | 0 |
| | Kerosene content | 0 | 0 | 0 | 0 | 0 |
| oxygen content (mass %) | | 0 | 0 | 18.2 | 13.8 | 36.4 |
| sulfur content (mass ppm) | | 8 | 9 | 0 | 0 | 0 |
| MTBE : methyl-t-butyl-ether TAE : t-amylethyl-ether MPA : methoxypropyl acetate | | | | | | |

Table 2

| | | Inventive Examples | | | | | | Comparative Examples | |
|------------------------|-----|--------------------|----|----|----|----|----|----------------------|-----|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 |
| Base gasoline Volume % | (A) | 95 | 90 | 85 | 85 | 85 | | 100 | |
| | (B) | | | | | | 85 | | 100 |
| | (C) | 5 | 10 | 15 | | | 15 | | |
| | (D) | | | | 15 | | | | |
| | (E) | | | | | 15 | | | |

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Table 2 (continued)

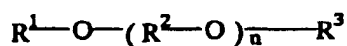
| | | Inventive Examples | | | | | | Comparative Examples | |
|-----------|--------------------------------------|--------------------|-------|-------|-------|-------|-------|----------------------|-------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 |
| 5 | oxygen content mass % | 0.9 | 1.8 | 2.7 | 2.9 | 6.7 | 1.8 | 0.0 | 0.0 |
| 10 | Distillation Properties to °C | | | | | | | | |
| | T ₁₀ | 48.5 | 49.0 | 50.5 | 54.5 | 52.5 | 52.0 | 48.5 | 51.5 |
| | T ₃₀ | 66.5 | 66.0 | 65.0 | 78.5 | 80.0 | 74.0 | 69.5 | 78.5 |
| | T ₅₀ | 94.5 | 88.0 | 84.5 | 101.0 | 112.0 | 108.5 | 98.0 | 111.5 |
| | T ₇₀ | 116.0 | 115.0 | 113.0 | 114.0 | 127.5 | 127.0 | 118.0 | 134.0 |
| | T ₈₀ | 140.5 | 140.0 | 138.0 | 136.5 | 141.0 | 158.5 | 140.0 | 162.5 |
| 15 | End Point | 175.0 | 176.0 | 175.5 | 176.0 | 164.0 | 173.0 | 174.5 | 176.0 |
| Aromatics | | 31.5 | 29.9 | 28.2 | 28.2 | 28.2 | 37.3 | 33.2 | 43.1 |
| Paraffins | | 54.7 | 51.8 | 49.0 | 49.0 | 49.0 | 41.0 | 57.6 | 49.1 |
| Olefins | | 8.7 | 8.3 | 7.8 | 7.8 | 7.8 | 6.7 | 9.2 | 7.8 |
| 20 | Composition Vol. % | | | | | | | | |
| 25 | V(Bz) | 0.7 | 0.6 | 0.6 | 0.6 | 0.6 | 0.5 | 0.7 | 0.5 |
| | V(Tol) | 12.6 | 12.0 | 11.3 | 11.3 | 11.3 | 9.4 | 13.3 | 11.2 |
| | V(C ₈ A) | 9.1 | 8.6 | 8.2 | 8.2 | 8.2 | 7.2 | 9.6 | 8.6 |
| | V(C ₉ A) | 8.6 | 8.1 | 7.7 | 7.7 | 7.7 | 19.5 | 9.0 | 21.9 |
| | V(C ₁₀ +A) | 0.6 | 0.5 | 0.5 | 0.5 | 0.5 | 0.8 | 0.6 | 0.9 |
| | V(MA)/V(PA) | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 | 1.7 | 1.9 | 1.6 |
| 30 | V(C ₄) | 8.4 | 7.9 | 7.5 | 7.5 | 7.5 | 6.3 | 8.8 | 7.5 |
| | V(C ₅ p) | 9.1 | 8.6 | 8.2 | 8.2 | 8.2 | 6.8 | 9.6 | 8.2 |
| | V(C ₅ o) | 5.2 | 5.0 | 4.7 | 4.7 | 4.7 | 3.9 | 5.5 | 4.7 |
| | V(C ₆ p) | 6.0 | 5.7 | 5.4 | 5.4 | 5.4 | 4.5 | 6.3 | 5.4 |
| | V(C ₆ o) | 3.5 | 3.3 | 3.1 | 3.1 | 3.1 | 2.6 | 3.7 | 3.1 |
| | V(C ₇ +p) | 31.3 | 29.6 | 28.0 | 28.0 | 28.0 | 23.4 | 32.9 | 28.0 |
| 35 | V(C ₉ +) kerosene content | 9.1 | 8.6 | 8.2 | 8.2 | 8.2 | 20.2 | 9.6 | 22.8 |
| | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| 40 | RON | 101.3 | 102.5 | 102.9 | 102.0 | 90.5 | 104.5 | 100.2 | 102.9 |
| | MON | 89.0 | 90.0 | 90.1 | 89.9 | 80.6 | 92.3 | 88.7 | 89.9 |
| 45 | RVP kPa | 76.0 | 77.5 | 77.5 | 74.5 | 72.0 | 72.0 | 75.0 | 70.0 |
| | density g/cm ³ | 0.756 | 0.755 | 0.755 | 0.769 | 0.792 | 0.776 | 0.757 | 0.775 |
| | sulfur content mass ppm | 7 | 8 | 8 | 7 | 8 | 7 | 8 | 9 |
| 50 | Unwashed existent gum mg/100mL | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| | washed existent gum mg/100mL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | oxidation stability | >1440 | >1440 | >1440 | >1440 | 1440> | >1440 | >1440 | >1440 |
| 55 | copper corrosion | 1A | 1A | 1A | 1A | 1A | 1A | 1A | 1A |
| | Automobile Test 1 smoke % | 4.7 | 2.9 | 1.8 | 3.3 | 2.8 | 4.8 | 6.5 | 9.3 |

Table 2 (continued)

| | Inventive Examples | | | | | | Comparative Examples | |
|--|--------------------|-----|-----|-----|-----|-----|----------------------|-----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 |
| Automobile Test 2 dilution by gasoline vol. % | 5.7 | 6.2 | 5.5 | 6.3 | 6.4 | 7.4 | 6.3 | 8.5 |

Claims

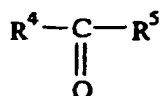
1. An unleaded gasoline for a direct injection gasoline engine which comprises an oxygen-containing compound having 2-15 carbon atoms in an amount in terms of oxygen atom of 0.1-15 mass % based on the total gasoline.
2. An unleaded gasoline according to claim 1 wherein said oxygen-containing compound has in its molecule at least one oxygen-containing group selected from the group consisting of a hydroxyl group, an ether bond and a carbonyl group.
3. An unleaded gasoline according to claim 1 wherein said oxygen-containing is represented by the formula



(I)

wherein R^1 and R^3 are each independently hydrogen or a $C_1 - C_{15}$ hydrocarbon group, R^2 is a $C_2 - C_4$ alkylene group and n is an integer of 0 - 7, provided that the total carbon number in the molecule is from 2 to 15 and if n is 0, it is excluded that both R^1 and R^3 are hydrogen at the same time.

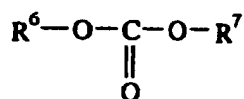
4. An unleaded gasoline according to claim 1 wherein said oxygen-containing compound is a ketone represented by the formula



(II)

wherein R^4 and R^5 are each independently a $C_1 - C_{13}$ hydrocarbon group, provided that the total carbon numbers of R^4 and R^5 are 2 - 14.

5. An unleaded gasoline according to claim 1 wherein said oxygen-containing compound is a cyclic ketone such as cyclohexane.
6. An unleaded gasoline according to claim 1 wherein said oxygen-containing compound is an ester.
7. An unleaded gasoline according to claim 6 wherein said ester is selected from the group consisting of methyl acetate, ethyl acetate, propyl acetate, butyl acetate, methoxypropyl acetate, dimethyl succinate, diethyl succinate, dimethyl malate and diethyl malate.
8. An unleaded gasoline according to claim 1 wherein said oxygen-containing compound is a carbonic ester represented by the formula



(III)

wherein R⁶ and R⁷ are each independently a C₁ - C₁₃ hydrocarbon group, provided that the total carbon numbers of R⁶ and R⁷ are 2 - 14.

9. An unleaded gasoline according to claim 8 wherein said carbonic ester is selected from the group consisting of dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, ethylpropyl carbonate, dipropyl carbonate, methylbutyl carbonate, ethylbutyl carbonate, propylbutyl carbonate, dibutyl carbonate, methylpentyl carbonate, ethylpentyl carbonate, propylpentyl carbonate, butylpentyl carbonate and dipentyl carbonate.
10. An unleaded gasoline according to claim 1 wherein said oxygen-containing compound is a cyclic ester such as γ -butyrolactone.
11. An unleaded gasoline according to claim 1 wherein the content of said oxygen-containing compound is in the range of 0.7 - 10 % by volume by oxygen atom conversion.
12. An unleaded compound according to claim 1 further containing detergent dispersants selected from the group consisting of succinic acid imide, polyalkyl amine and polyether amine.



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